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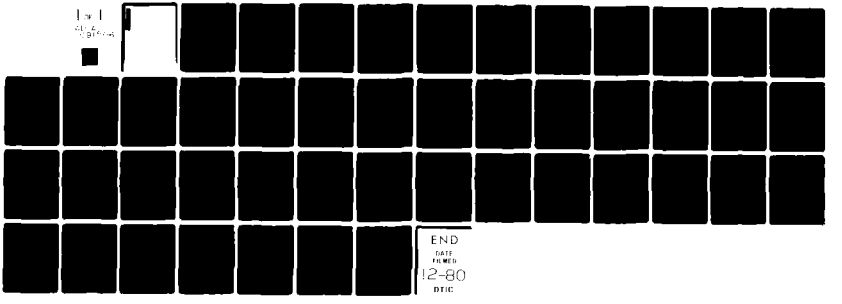

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A comprehensive quantum mechanical theory of atomic spectral line shapes is developed within the framework of the Lippmann - Schwinger scattering theory adapted to the tetradic (Liouville) - space representation of density matrices. An expression for the spontaneous electric-dipole emission rate is derived which has the same general form as the results obtained by Baranger and by Kolb and Griem for overlapping lines. The frequency-dependent relaxation operator which occurs in this expression involves not only the collisional broadening interaction but also the interactions which give rise to autoionization and to both spontaneous and induced

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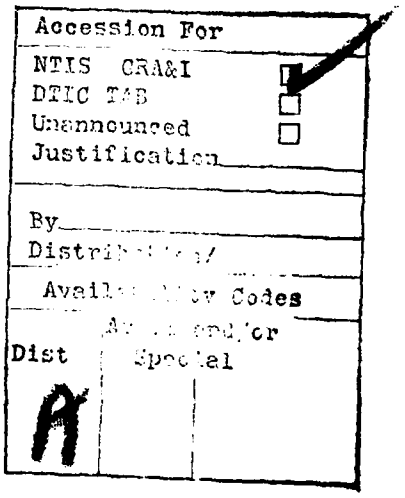
20. radiative transitions. Explicit expressions for the widths are obtained in the isolated-line approximation by evaluating the lowest-order nonvanishing contribution to the diagonal matrix elements of the relaxation operator. The total width is obtained as the sum of the rates for all inelastic transitions from the initial and final states comprising the spectral line and the term involving the square of the difference between the elastic scattering amplitudes. Finally, we present a qualitative discussion on how the partial widths vary with the states comprising the spectral line and with the physical properties of the surrounding particles and radiation field.

CONTENTS



THE BRAODENING OF SPECTRAL LINES BY AUTOIONIZATION, RADIATIVE TRANSITIONS, AND COLLISIONS

I. INTRODUCTION

The shape of atomic spectral lines is seldom determined exclusively by the spontaneous radiative or autoionization processes. In addition to the Doppler effect, spectral lines can be appreciably broadened as a result of collisions with the surrounding particles, classical electromagnetic fields, and radiation fields. Although natural broadening is neglected in most theories of collision or pressure broadening, it is desirable to have a comprehensive theoretical framework in which all broadening mechanisms can be treated on an equal footing. Such a theory could be applied to calculate the shapes of satellite lines which are associated with resonance lines of multiply-charged ions in the x-ray emission spectra of high-temperature plasmas. Since the satellite lines are prominent features over a wide range of electron densities (10^{10} - 10^{24} cm^{-3}), it is desirable to take into account their natural width due to spontaneous radiative decay and autoionization. Another application of a more general theory would be the simultaneous treatment of collision and radiation broadening.

Most treatments of collision or pressure broadening are based on the evaluation of the autocorrelation function of the dipole-moment operator. The modern quantum theory of spectral line broadening by plasmas has been developed from this point of view by Baranger[1-3] and independently by Kolb and Griem[4]. Collision broadening by neutral gases has been treated by Fano[5] using a variation of the autocorrelation-function approach which is directly applicable to other broadening mechanisms. The key quantity in Fano's treatment is the frequency-dependent relaxation operator introduced by Zwanzig[6]. This operator obeys a Lippman-Schwinger type equation which is defined in the Liouville-space

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representation, in which density matrices are described by vectors. In the present investigation, we derive the general form of the overlapping line-shape formula[1-4] by evaluating the Liouville-space expression for the spontaneous electric-dipole emission rate between states of the complete quantum mechanical system, which consists of the atomic system, the surrounding particles, and the radiation field. The key quantity in this treatment is the Liouville-space scattering operator, employed in the investigations of Ben-Reuven and co-workers[8-10], which is defined in terms of the Zwanzig relaxation operator.

The determination of the spectral line shape is reduced to the problem of evaluating the matrix elements of the relaxation operator, whose real and imaginary parts correspond to the line shifts and widths, respectively. In this investigation, the explicit expressions for the widths are obtained in the isolated-line approximation by evaluating the lowest-order nonvanishing contribution to the diagonal matrix elements of the relaxation operator. We show that the total width is the sum of the rates for all inelastic transitions from the initial and final atomic states comprising the spectral line and a term involving the square of the difference between the elastic scattering amplitudes. In a treatment of the isolated line shape problem based on the autocorrelation function, Lambropoulos[11] obtained only the inelastic contributions and did not allow for autoionization processes.

The remainder of this paper is organized as follows: In section II, we review the general theory of transition probabilities within the framework of the density matrix description of atomic states. In section III, the spontaneous emission rate for electric-dipole radiation is evaluated and shown to have the same form as the general formula for overlapping lines. In section IV, explicit expressions are obtained for the widths associated with various broadening mechanisms in the isolated-line approximation. The variations of these widths

with the atomic states and with the properties of the surrounding particles and radiation field are discussed in section V.

II. DENSITY MATRIX DESCRIPTION

A very general theory of transition probabilities can be developed within the framework of the density matrix description of states in quantum mechanics[7]. In order to describe radiative transitions of an atomic system which is interacting with the surrounding particles through collisions, it is necessary to first consider the total Hamiltonian

$$H = H^S + H^P + H^R + V^{SP} + V^{SR} + V^{PR} , \tag{1}$$

where H^S is the Hamiltonian for the isolated atomic system, H^P is the Hamiltonian for the perturbing particles, and H^R is the Hamiltonian for the free radiation field. The interaction between the atomic system and the surrounding particles is represented by V^{SP}, while the interaction between the atomic system and the radiation field is denoted by V^{SR}. The interaction V^{PR}, which describes radiation processes involving the perturbing particles, is usually neglected in the theory of spectral line shapes. However, a treatment of perturber radiation interfering with line radiation has been given by Burgess[12].

Eigenstates of H^S, H^P, and H^R will be denoted by $|a\rangle$, $|b\rangle$, ..., $|p\rangle$, $|q\rangle$, ..., and $|n\rangle$, $|m\rangle$ ..., respectively. The index p represents the quantum states of all the surrounding particles, and the index n is understood to represent a set of photon occupation numbers, one for each mode of the radiation field. The notation can be further compressed by introducing the single index α to represent a, p, n; and the index β for b, q, m, etc. We shall assume that the zero-order Hamiltonian eigenvalue problem

$$H^o \, | \, \alpha \rangle = \hbar \, \omega_\alpha \, | \, \alpha \rangle \ , \tag{2}$$

where

$$H^o = H^S + H^P + H^R, \tag{3}$$

can be solved. The solution of (2) can be most easily obtained if correlations between the perturbing particles are neglected. In the theory of spectral line broadening by plasmas[13], $|a\rangle$ and $|b\rangle$ are often taken to be eigenstates of the atomic system in the presence of the electric-microfield produced by the plasma ions, which is usually assumed to be time-dependent on the time scale of the radiative transition. In order to describe autoionization, part of the electrostatic interaction between the atomic electrons must be removed from H^S and included in equation (6) below.

A general eigenstate of H^o can be represented by the density operator

$$\rho_i = \rho^S \times \rho^P \times \rho^R \tag{4}$$

for the initial state. The separable form implies that initially there are no correlations between the atomic system, the perturbing particles, and the radiation field. The matrices corresponding to ρ^S, ρ^P, and ρ^R are assumed to be diagonal in the representations a, p, and n, respectively. For example, the atomic density matrix ρ^S can then be expanded in the form

$$\rho^S = \sum_a \rho_a \; |a\rangle\langle a| . \tag{5}$$

In order to describe the transitions between the eigenstates of H^o which are induced by the interaction

$$V = V^{SP} + V^{SR} + V^{PR} , \tag{6}$$

it is necessary to investigate the time evolution of the density operator $\rho(t)$ for the complete interacting system. After introducing the Liouville-space operator

$$\mathcal{L} = \hbar^{-1} (H\, I^* - I\, H^*), \tag{7}$$

the Schrodinger equation can be written in the form[5]

$$\frac{d}{dt}\ \rho(t) = -\,i\,\mathcal{L}\,\rho(t). \tag{8}$$

The matrix elements of equation (8) are given by

$$\frac{d}{dt}\ \rho_{ab}\ (t) = -\,i \sum_{cd} \mathcal{L}_{ab,cd}\ \rho_{cd}(t) \tag{9}$$

where

$$\mathcal{L}_{ab,cd} = \hbar^{-1}\ (H_{ac}\ \delta_{bd} - \delta_{ac}\ H^{*}_{bd})\ . \tag{10}$$

The asterisk denotes complex conjugation. The solution to equation (8) can be expressed formally by

$$\rho\,(t) = \mathcal{U}\ (t,t_o)\ \rho(t_o)\ , \tag{11}$$

where $\mathcal{U}\ (t,t_o)$ is the Liouville time-evolution operator defined by

$$\mathcal{U}\,(t,t_o) = \exp\left[-i\,\mathcal{L}\ (t-t_o)\right]\ . \tag{12}$$

In order to define the transition probability, it is necessary to introduce the final state projection operator P_f. The spontaneous emission of a single photon with wave number $\vec{k}$ and polarization λ can be described by the final state projection operator

$$P_f = \sum_b \left| b\right\rangle\left\langle b \right| \times \left|1_{\vec{k}\ \lambda}\right\rangle\left\langle 1_{\vec{k}\ \lambda}\right| \times I_B\ , \tag{13}$$

where I_B is the unit operator in all other degrees of freedom which will be treated as bath states, to be defined below. The probability per unit time for the transition $i \to f$ can then be expressed by[10]

$$A(i \to f) = \lim_{t \to \infty}\ \frac{d}{dt}\ \lim_{t_o \to -\infty}\ \mathrm{Tr}\left\{P_f\,\mathcal{U}\ (t,t_o)\ \rho_i\ (t_o)\right\} \tag{14}$$

which is the Liouville-space analogue of the definition given by Goldberger and Watson[14].

Equation (14) provides a general description of a collision process in which the asymptotic states are eigenstates of the Hamiltonian H^o for the non-interacting systems. It has been pointed out[9] that the same description can be applied to relaxation processes which involve an initial stationary state (e.g. a state with only diagonal non-zero density matrix elements).

The asymptotic time limits can be taken to obtain the steady-state transition rate[10]

$$A(i \to f) = - i \, \mathrm{Tr} \left\{ P_f \, \mathcal{T}(+ i 0) \, \rho_i \right\} . \tag{15}$$

The Liouville operator $\mathcal{T}(z)$ is the tetradic-space analogue of the T matrix occurring in ordinary scattering theory. The Liouville-space analogue of the Lippman-Schwinger equation can be written in the form

$$\mathcal{T}(z) = \mathcal{V} + \mathcal{V} \mathcal{H}(z) \mathcal{V} , \tag{16}$$

where $\mathcal{H}(z)$ is the Green's operator

$$\mathcal{H}(z) = (z - \mathcal{L})^{-1} . \tag{17}$$

The Liouville operator $\mathcal{L}$ has been divided according to

$$\mathcal{L} = \mathcal{L}^o + \mathcal{V}, \tag{18}$$

where $\mathcal{L}^o$ and $\mathcal{V}$ are the Liouville operators corresponding to H^o and V, respectively. The limit $z \to i 0$ of the complex variable z in equation (15) corresponds to reaching the origin from above the real axis. The initial state density operator ρ_i and the final state projection operator P_f in equation (15) must correspond to stationary states of $\mathcal{L}^o$, i.e.

$$\mathcal{L}^o \rho_i = \mathcal{L}^o P_f = 0 \tag{19}$$

In the density matrix formulation of relaxation processes[6,9,10], the transition amplitude is expressed in terms of a scattering operator $\mathcal{T}^r(z)$, which is defined on a subspace of states incorporating only the interaction between the uncorrelated atomic system and the relevant mode $\vec{k}\lambda$ of the radiation field. The scattering operator $\mathcal{T}^r(z)$ is then explicitly expanded in a power series of the relevant interaction $\mathcal{V}^r$. The remaining interactions are introduced as relaxation effects by a self-energy operator. The distinction between the "free" states of the relevant degrees of freedom and the states in which they are correlated to the remaining (b_{ath}) degrees of freedom can be formally achieved by using the Liouville-space projection operators $\mathcal{P}$ and $\mathcal{Q} = 1 - \mathcal{P}$ which were introduced by Zwanzig[6]. These projection operators play a role similar to that of the dyadic projection operators introduced in the theory of nuclear reactions by Feshbach[15]. Their precise definition will be given below later.

The relevant part of the interaction can be defined by

$$\mathcal{V}^r = \mathcal{P}\mathcal{V}^{SR}_{\vec{k}\lambda}\mathcal{P}. \tag{20}$$

The relevant scattering operator $\mathcal{T}^r(z)$ obeys the Lippmann-Schwinger type equation

$$\mathcal{T}^r(z) = \mathcal{V}^r + \mathcal{V}^r \mathcal{H}^r(z)\, \mathcal{V}^r, \tag{21}$$

where

$$\mathcal{H}^r(z) = \left[z - \mathcal{P}\mathcal{L}^o\mathcal{P} - \mathcal{P}\mathcal{K}(z)\mathcal{P}\right]^{-1}. \tag{22}$$

The self-energy operator $\mathcal{K}(z)$ is given by

$$\mathcal{K}(z) = \mathcal{V} + \mathcal{V}\mathcal{Q}(z - \mathcal{Q}\mathcal{L}\mathcal{Q})^{-1}. \tag{23}$$

Equations (22) and (23) are analogous to the results obtained for the ordinary (dyadic) Greens operator by Mower[16]. The transition rate can be evaluated in terms of $\mathcal{T}^r(+\,i\,0)$ as follows[10].

$$A(i \to f) = - i \, \mathrm{Tr} \left\{ P_f \, \mathcal{T}^r(+ i 0) \, \rho_i \right\}. \tag{24}$$

The Zwanzig projection operator can be defined in the double-space notation introduced by Baranger[1-3] as follows:

$$\mathcal{P} = | \rho_B \rangle\rangle\langle\langle I_B | , \tag{25}$$

where B denotes the bath degrees of freedom. The effect of $\mathcal{P}$ on a Liouville operator is to average it over these degrees of freedom. The double-space vectors in the subspace spanned by $\mathcal{P}$ will be denoted by $| a b, n m \rangle\rangle$, where $| a b \rangle\rangle$ represents the operator $| a \rangle\langle a |$ in the space of eigenstates of H^S and $| n m \rangle\rangle$ represents $| n \rangle\langle m |$ in the space of relevant photon occupation number states. The initial state density operator ρ_i^r and the final state projection operator P_f^r, which are defined on the relevant degrees of freedom, can be expanded in the form

$$\rho_i^r = \sum_a \rho_a \, | a a, 0 0 \rangle\rangle \tag{26}$$

and

$$P_f^r = \sum_b | b b, 1 1 \rangle\rangle . \tag{27}$$

The single-photon spontaneous emission rate can now be expressed in terms of the matrix elements of $\mathcal{T}^r(+ i 0)$ as follows:

$$A(i \to f) = - i \langle\langle P_f | \mathcal{T}^r (+ i 0) | \rho_i \rangle\rangle$$

$$= - i \sum_a \sum_b \langle\langle b b, 1 1 | \mathcal{T}^r (+ i 0) | a a, 0 0 \rangle\rangle \rho_a . \tag{28}$$

The summations over a and b are to be taken over all bound and continuum states of the atomic system. In practice, these summations are restricted to include only a few discrete states.

III. SPONTANEOUS EMISSION OF ELECTRIC-DIPOLE RADIATION

In this section, we evaluate the spontaneous emission rate for single-photon electric-dipole radiation. The objective of this evaluation is to demonstrate that the formula for overlapping lines[1-5], which is usually obtained by starting with the autocorrelation function of the electric-dipole moment operator, can be derived from the general equantum mechanical expression for the transition rate in the Liouville-space representation of density matrices. Alternative density matrix formulations of the line shape problem have been given by Cooper[17] and Davis[18]. In these formulations the time dependence of the density matrix is treated directly.

Since the second term in equation (21) gives the only nonvanishing contribution to the scattering operator $\mathcal{T}^{r}(z)$, the rate for the spontaneous emission of dipole radiation is given by

$$
\begin{aligned}
A_r(\omega) &= -i \sum_a \sum_b \\
&\times \langle\langle bb, 11 | \mathcal{V}^r \mathcal{H}^r(+i0) \mathcal{V}^r | a\,a, 0\,0 \rangle\rangle \rho_a \\
&= -i \sum_a \sum_b \rho_a \sum_{c n_c} \sum_{d n_d} \sum_{e n_e} \sum_{f n_f} \\
&\times \langle\langle bb, 11 | \mathcal{V}^{SR}_{\vec{k}\lambda} | c\,d, n_c\ n_d \rangle\rangle \\
&\times \langle\langle cd, n_c\ n_d | \mathcal{H}^r(+i0) | e\,f, n_e\ n_f \rangle\rangle \\
&\times \langle\langle ef, n_e\ n_f | \mathcal{V}^{SR}_{\vec{k}\lambda} | a\,a, 0\,0 \rangle\rangle ,
\end{aligned}
\tag{29}
$$

where all summations over the relevant degrees of freedom are indicated explicitly in the second version.

The matrix elements of the Liouville interaction operator $\mathcal{V}^{SR}_{\vec{k}\lambda}$ can be evaluated using the definition which follows from equation (7). The matrix elements of the dyadic interaction operator $V^{SR}_{\vec{k}\lambda}$ are evaluated using the expansion

$$V^{SR}_{\vec{k}\lambda} \mid a, n \rangle = \sum_b \left\{ V_{ba}(\vec{k}) \sqrt{n} \mid b, n-1 \right\rangle + V_{ba}(-\vec{k}) \sqrt{n+1} \mid b, n+1 \rangle \Big\} , \tag{30}$$

where

$$V_{ba}(\vec{k}) = -\frac{e}{m} \sqrt{\frac{2\pi\hbar}{\omega}} \left\langle b \mid \sum_j \hat{\varepsilon}_\lambda \cdot \vec{p}_j \; e^{i\vec{k}\cdot\vec{r}} \mid a \right\rangle . \tag{31}$$

We then obtain the result

$$\langle\langle e f, n_e n_f \mid \mathcal{V}^{SR}_{\vec{k}\lambda} \mid a a, 0 0 \rangle\rangle = \hbar^{-1} \left\{ V_{ea}(-\vec{k}) \, \delta_{n_e, 1} \, \delta_{f,a} \, \delta_{n_f, 0} - \delta_{e,a} \, \delta_{n_e, 0} \, V^*_{fa}(-\vec{k}) \, \delta_{n_f, 1} \right\} . \tag{32}$$

We obtain a similar expression for $\langle\langle \; bb, 11 \mid \mathcal{V}^{SR}_{\vec{k}} \mid cd, n_c n_d \rangle\rangle$, except for the presence of terms corresponding to n_c or $n_d = 2$. These terms can be neglected because they do not contribute to the dominant spontaneous emission process.

The frequency-dependent transition rate $A_r(\omega)$ given by equation (29) can now be written as a sum of four terms. These terms may be combined in pairs by utilizing the Hermitian property

$$V_{ab}(\vec{k}) = V^*_{ba}(\vec{k}) \tag{33}$$

and the Liouville conjugation symmetry relationship[9]

$$\mathcal{H}_{ab,\,cd}(z) = -\,\mathcal{H}^{*}_{ba,\,dc}(-z^{*}), \tag{34}$$

which is a consequence of the microscopic reversibility of the time evolution operator under time reversal.

The frequency-dependent transition rate can now be written in the form

$$A_r(\omega) = -\,\frac{2}{\hbar^2}\,\mathrm{Im}\sum_a\sum_b\sum_c\sum_d V_{db}(\vec{k})\,\mathcal{H}_{bd,\,ac}(\omega)\,V_{ac}(\vec{k})\,\rho_a$$

$$= -\,\frac{2}{\hbar^2}\,\mathrm{Im}\,\mathrm{Tr}\left[V(\vec{k})\,\mathcal{H}(\omega)\,\rho\,V(\vec{k})\right], \tag{35}$$

where the reduced Green's operator $\mathcal{H}(\omega)$ is defined by

$$\mathcal{H}_{bd,\,ac}(\omega) = \langle\langle\, bd,\,0\,1\,|\,\mathcal{H}^{r}(+\,i\,o)\,|\,ac,0\,1\,\rangle\rangle - \langle\langle\, bd,\,1\,0\,|\,\mathcal{H}^{r}(+\,i\,o)\,|\,ac,0\,1\,\rangle\rangle. \tag{36}$$

The second term, in which the photon occupation numbers are interchanged in the bra, does not give a sharp resonant contribution to the spectral line shape and will therefore be omitted.

Using the relationship

$$\mathcal{P}\,\mathcal{L}^{\circ}\,\mathcal{P}\,|\,ab,\,nm\,\rangle\rangle = \left[\omega_a - \omega_b + (n-m)\,\omega\right]\,|\,ab,\,nm\,\rangle\rangle \tag{37}$$

and neglecting the relaxation operator $\mathcal{R}$, the reduced tetradic Greens operator generally defined by equation (36) has matrix elements given by

$$\mathcal{H}_{bd,\,ac}(\omega) = \lim_{\eta\to o}\,(\omega_c - \omega_a + \omega + i\,\eta)^{-1}\,\delta_{ba}\,\delta_{dc}. \tag{38}$$

Consequently, the frequency-dependent transition rate in the absence of relaxation effects simplifies to

$$A_r(\omega) = \frac{2\pi}{\hbar^2} \sum_a \sum_b | V_{a\,b} (\vec{k}) |^2 \rho_a \delta(\omega - \omega_a + \omega_b) , \qquad (39)$$

which is the familiar Fermi Golden Rule formula for spontaneous emission from the levels a to the levels b.

In order to obtain the differential transition rate for the emission of a photon per unit solid angle and angular frequency intervals, equation (35) must be multiplied by the density of final states factor $\omega^2/(2\pi c)^3$. This factor would have been introduced automatically if the final state projection operator (27) had been more carefully defined to take into account the continuous distribution of modes of the radiation field. Using the electric-dipole approximation

$$V_{b\,a} (\vec{k}) = - i \sqrt{2\pi\hbar\omega} \left\langle b \mid \vec{D}_\lambda \mid a \right\rangle , \qquad (40)$$

where D_λ denotes the component of the total atomic dipole-moment operator in the direction of polarization, the differential photon emission rate for a given polarization λ is obtained in the form

$$A_r^\lambda (\omega,\Omega) = \frac{\omega^3}{2\pi\hbar c^3} L_\lambda (\omega,\Omega) . \qquad (41)$$

The line shape function $L_\lambda (\omega,\Omega)$, which depends on the angles Ω of photoemission, is given by

$$L_\lambda (\omega,\Omega) = -\frac{1}{\pi} \mathrm{Im}\ \mathrm{Tr} \left[D_\lambda \mathcal{H}(\omega) \rho D_\lambda \right] . \qquad (42)$$

Usually, one is interested only in the total spontaneous emission rate per unit frequency interval

$$A_r(\omega) = \sum_\lambda \int d\Omega\ A_r{}^\lambda (\omega,\Omega) = \frac{4}{3} \frac{\omega^3}{\hbar c^3} L(\omega), \qquad (43)$$

where

$$L(\omega) = - \frac{1}{\pi} \mathrm{Im}\ \mathrm{Tr} \left[\vec{D} \cdot \mathcal{H}(\omega) \rho \cdot \vec{D} \right] . \qquad (44)$$

Equation (44) has the same form as the results derived by Baranger[1-3], by Kolb and Griem[4], and by Fano[5]. Note, however, that equation (44) is more general than the formula usually employed for overlapping lines[13] in that no restriction has as yet been imposed on the subspace of the atomic states over which the trace is to be taken. Consequently, equation (44) provides a general framework for the description of the entire emission spectrum due to all bound-bound transitions, including transitions involving autoionizing levels.

IV. The Isolated Line Approximation

If only the diagonal matrix elements $\mathcal{L}_{ab,\,ab}(\omega)$ of the reduced Green's operator $\mathcal{L}(\omega)$ are included in the line shape formula (44), we obtain

$$L(\omega) = -\frac{1}{\pi}\,\mathrm{Im}\sum_a\sum_b \frac{|\vec{D}_{ab}|^2\,\rho_a}{\omega-\omega_a+\omega_b-\mathcal{R}_{ab,\,ab}(\omega)}\,, \tag{45}$$

where

$$\mathcal{R}_{ab,\,ab}(\omega) = \left\langle\!\left\langle ab,\,0\,1\,|\,\mathcal{P}\,\mathcal{R}(+i0)\,\mathcal{P}\,|\,ab,\,0\,1\right\rangle\!\right\rangle. \tag{46}$$

From the definition of the tetradic relaxation operator $\mathcal{R}(z)$ given by equation (23), it follows that

$$\mathcal{R}^{+}(z) = \mathcal{R}(z^*)\,, \tag{47}$$

where the Hermitian conjugation of $\mathcal{R}$ is defined by

$$(\mathcal{R}^{+})_{\alpha\beta,\,\alpha'\beta'} = \mathcal{R}^{*}_{\alpha'\beta'\alpha\beta}\,. \tag{48}$$

Consequently, the procedure of Goldberger and Watson[14] can be followed to obtain

$$\lim_{\eta \to o} \mathcal{R}(x \pm i\eta) = \Delta(x) \mp i \Gamma(x) \,|\, 2, \tag{49}$$

where $\Delta(x)$ and $\Gamma(x)$ are Hermitian operators. $\mathcal{R}_{ab,ab}(\omega)$ can therefore be expressed in the form

$$\mathcal{R}_{ab,ab}(\omega) = \Delta_{ab,ab}(\omega) - i\,\Gamma_{ab,ab}(\omega) \,|\, 2, \tag{50}$$

where $\Delta_{ab,ab}(\omega)$ gives the shift associated with the line $a \to b$ and $\Gamma_{ab,ab}(\omega)$ corresponds to the full-width at half maximum.

It is clear that equation (45) corresponds to an incoherent superposition of the Lorentzian profiles associated with each atomic line $a \to b$. The isolated line approximation is expected to be valid provided that the separations of the lines are large compared with their widths. In this section, we evaluate the lowest-order nonvanishing contributions to the widths arising from autoionization, spontaneous and induced radiative transitions, and collisions.

The width and shift operators $\Gamma(x)$ and $\Delta(x)$ can be expressed in terms of the relaxation operator $\mathcal{R}(x + i\eta)$ by following the procedure used by Goldberger and Watson[14]. From the definition (23) and the identity

$$(z - \mathcal{Q}\mathcal{L}\mathcal{Q})^{-1}\mathcal{Q}\mathcal{V} = (z - \mathcal{Q}\mathcal{L}^{o}\mathcal{Q})^{-1}\mathcal{Q}\mathcal{R}(z), \tag{51}$$

which is analogous to the dyadic relationship used by Mower[16], we obtain the results

$$\Gamma(x) = 2\pi \lim_{\eta \to o} \left[\mathcal{R}^{+}(x + i\eta)\,\mathcal{Q}\,\delta(x - \mathcal{Q}\mathcal{L}^{o}\mathcal{Q})\,\mathcal{Q}\mathcal{R}(x + i\eta) \right] \tag{52}$$

and

$$\Gamma(x) = \mathcal{R}_{e}\mathcal{V} - \frac{P}{2\pi}\int_{-\infty}^{\infty} \frac{\Gamma(x')\,dx'}{x' - x}, \tag{53}$$

where P denotes the Cauchy principal value. Similar results have also been derived by Lambropoulos[11].

The lowest-order nonvanishing contribution to the width operator $\Gamma(x)$, which is obtained from the approximation of $\mathcal{R}(z)$ by $\mathcal{V}$, is

$$\Gamma(z) = 2\pi \mathcal{V} Q \delta(x - Q\mathcal{L}^{\circ} Q) Q\mathcal{V} . \tag{54}$$

Using the compressed notation introduced in section II for the eigenstates of $\mathcal{L}^{\circ}$, the general matrix elements of $\Gamma(x)$ can be expressed in the form

$$\begin{aligned}
\langle\langle \alpha\ \beta \mid \Gamma(x) \mid \alpha'\ \beta' \rangle\rangle &= \frac{2\pi}{\hbar^2} \sum_{\alpha''\ \beta''} \delta(x-\omega_{\alpha''} + \omega_{\beta''}) \\
\times & \langle\langle \alpha\ \beta | VI^* - IV^* | \alpha''\ \beta'' \rangle\rangle \langle\langle \alpha''\ \beta'' | V\ I^* - I\ V^* | \alpha'\ \beta' \rangle\rangle \\
= & \frac{2\pi}{\hbar^2} \sum_{\alpha''}{}' V_{\alpha\,\alpha''} V_{\alpha''\,\alpha'} \delta_{\beta\,\beta'} \delta(x - \omega_{\alpha''} + \omega_{\beta}) \\
+ & \frac{2\pi}{\hbar^2} \sum_{\beta''} V^*_{\beta\,\beta''} V^*_{\beta''\,\beta'} \delta_{\alpha\,\alpha'} \delta(x - \omega_{\alpha} + \omega_{\beta''}) \\
- & \frac{2\pi}{\hbar^2} V_{\alpha\,\alpha'} V^*_{\beta\,\beta'} \delta(x - \omega_{\alpha'} + \omega_{\beta}) \\
- & \frac{2\pi}{\hbar^2} V_{\alpha\,\alpha'} V^*_{\beta\,\beta'} \delta(x - \omega_{\alpha} + \omega_{\beta'}) ,
\end{aligned} \tag{55}$$

where we have made the approximation $Q = 1$, discussed by Ben-Reuven[19].

To obtain the line width, we must evaluate the expression

$$\Gamma_{a\,b,\,a\,b}(\omega) = \langle\langle a\,b,\,0\,1 \mid \mathcal{P}\Gamma(+i0)\ \mathcal{P} \mid a\,b,\,0\,1 \rangle\rangle , \tag{56}$$

It is now necessary to introduce the bath degrees of freedom n and p, where n represents the set of all photon occupation numbers and p is the quantum state of the perturbing particles. The frequency-dependent width can then be expressed in the form

$$\Gamma_{ab,ab}(\omega) = \sum_{n} \sum_{n'} \sum_{p} \sum_{p'} \langle\langle ab, 01, n\,n\;p\,p \,|\, \Gamma(0) \,|\, ab, 01, n'n', p'p' \rangle\rangle \; \rho'_n \; \rho'_p . \tag{57}$$

It is necessary to make the somewhat artificial distinction between the relevant and bath photon modes in order to obtain the frequency-dependence, which occurs in the delta functions in equation (55). In subsequent equations, reference to the relevant photon mode numbers will be omitted whenever it becomes unnecessary. After substituting equation (55) into equation (57), the lowest-order non-vanishing contribution to the isolated line width can be obtained in the form

$$\begin{aligned}
\Gamma_{ab,ab}(\omega) = {} & \frac{2\pi}{\hbar^2} \sum_{a'' \neq a} \sum_{n} \sum_{n''} \sum_{p} \sum_{p''} | \langle a\,n\,p \,|V|\, a''\,n''\,p'' \rangle |^2 \\
& \times \delta(\omega - \omega_{a''} + \omega_b - \omega_{p''} + \omega_p - \omega_{n''} + \omega_n) \; \rho_n \rho_p \\
& + \frac{2\pi}{\hbar^2} \sum_{b'' \neq b} \sum_{n} \sum_{n''} \sum_{p} \sum_{p''} | \langle b\,n\,p \,|V|\, b''\,n''\,p'' \rangle |^2 \\
& \times \delta(\omega - \omega_a + \omega_{b''} - \omega_p + \omega_{p''} - \omega_n + \omega_{n''}) \; \rho_n \rho_p \\
& + \frac{2\pi}{\hbar^2} \sum_{p} \sum_{p'} | \langle a\,p \,|V|\, a\,p' \rangle - \langle b\,p \,|V|\, b\,p' \rangle |^2 \\
& \times \delta(\omega - \omega_a + \omega_b - \omega_{p'} + \omega_p) \; \rho_{p'} \; .
\end{aligned} \tag{58}$$

The first two terms describe all inelastic transitions from the initial and final states of the radiating atomic system. Note that the states of the radiation field are not involved in the last term, which describes only elastic collisions. This is a consequence of the assumption that photons are emitted only by the atomic system and the neglect of correlations between the atomic system and the perturbers. The radiation emitted by the perturbers can be described by the use of higher-order perturbation theory.

A. Autoionization

Autoionization results form the electrostatic interaction V^S between a discrete state and the continuum states of the atomic system having the same energy. The definition of the zero-order atomic states can be made in an unambiguous manner by using the dyadic projection operators introduced by Feshbach[15] or by the alternative procedure introduced by Fano[20]. Autoionization can be included in the present theory by transferring V^S from H^o to V, as discussed in Section II. The width arising from the possibility of autoionization from both the initial and final states of the radiating atomic system is obtained from the inelastic terms in equation (58) and can be written as

$$\Gamma^A_{ab,ab}(\omega) = \frac{2\pi}{\hbar^2} \sum_c |\langle a | V^S | c \rangle|^2 \delta(\omega - \omega_c + \omega_b) + \frac{2\pi}{\hbar^2} \sum_c |\langle b | V^S | c \rangle|^2 \delta(\omega - \omega_a + \omega_c), \quad (59)$$

where the sum over c ranges over all continuum states which are allowed by the energy and symmetry selection rules. If we now make the approximation $\omega = \omega_a - \omega_b$, in which the frequency-dependence is neglected, we obtain the result

$$\Gamma^{A}_{ab,\,a\cdot b} = \frac{2\pi}{\hbar^2} \sum_{c} \left| \left\langle a \left| V^{S} \right| c \right\rangle \right|^2 \delta(\omega_a - \omega_c)$$

$$+ \frac{2\pi}{\hbar^2} \sum_{c} \left| \left\langle a \left| V^{S} \right| c \right\rangle \right|^2 \delta(\omega_b - \omega_c) \,, \tag{60}$$

which is the sum of the autoionization rates from the initial and final atomic levels. In its most general form, equation (60) gives the autoionization contribution to the line width for a radiative transition between two autoionizing levels a and b.

It is well-known that the mixing between the discrete and continuum states produces an asymmetric profile[20]. However, to the best of the authors knowledge, no theories have been developed which incorporate the effects of radiative transitions and collisions into the asymmetric line shape function. In the limit where the line profile parameter q introduced by Fano[20] becomes large, the line shape function approaches a Lorentzian function, which is generalized in the present investigation in order to treat all broadening mechanisms on an equal footing.

B. Radiative Transitions

The width arising from all radiative transitions from the states a and b which is obtained from the inelastic terms in equation (58) is given by

$$\Gamma^{(R)}_{ab,\,a\,b}(\omega) = \frac{2\pi}{\hbar^2} \sum_{a'' \neq a} \sum_{n''} \sum_{n} \left| \left\langle a\,n \left| V^{SR} \right| a''n'' \right\rangle \right|^2$$

$$\times \delta\,(\omega - \omega_{a''} + \omega_b - \omega_{n''} + \omega_n)\ \rho_n \tag{61}$$

$$+ \frac{2\pi}{\hbar^2} \sum_{b'' \neq b} \sum_{n''} \sum_{n} \left| \left\langle b\,n \left| V^{SR} \right| b''\,n'' \right\rangle \right|^2$$

$$\times \delta\,(\omega - \omega_a + \omega_{b''} - \omega_n + \omega_{n''})\ \rho_n \,.$$

We now introduce the expansion of the interaction V^{SR} in terms of modes $\vec{k}\lambda$ of the radiation field and replace the summation over $\vec{k}$ in this expansion by integrations over the frequency ω_k and the solid angle Ω_k. In the electric-dipole approximation, the total radiative contribution to the width is given by

$$\Gamma^{R}_{ab,\,ab}(\omega) = \frac{1}{2\pi\hbar c^3} \sum_{\lambda} \int\int \omega_k \, d\omega_k \, d\Omega_k$$

$$\times \Bigg\{ \sum_{a'' \neq a} \left| \langle a \,|\, D_\lambda \,|\, a'' \rangle \right|^2 (\omega_a - \omega_{a''})^2 \Big[\delta(\omega - \omega_{a''} + \omega_b - \omega_k)$$

$$+ \langle n_\lambda(\omega_k, \Omega_k) \rangle \; \delta(\omega - \omega_{a''} + \omega_b - \omega_k) \tag{62}$$

$$+ \langle n_\lambda(\omega_k, \Omega_k) \rangle \; \delta(\omega - \omega_{a''} + \omega_b + \omega_k) \Big]$$

$$+ \sum_{b'' \neq b} \left| \langle b \,|\, D_\lambda \,|\, b'' \rangle \right|^2 (\omega_b - \omega_{b''})^2 \Big[\delta(\omega - \omega_a + \omega_{b''} + \omega_k)$$

$$+ \langle n_\lambda(\omega_k, \Omega_k) \rangle \; \delta(\omega - \omega_a + \omega_{b''} + \omega_k)$$

$$+ \langle n_\lambda(\omega_k, \omega_k) \rangle \; \delta(\omega - \omega_a + \omega_{b''} - \omega_k) \Big] \Bigg\} ,$$

where $\langle n_\lambda(\omega_k, \Omega_k) \rangle$ denotes the average number of photons per unit frequency, per unit solid angle, which have polarization λ.

The contribution from all spontaneous radiative transitions can be obtained from the terms which are independent of the average number of photons by performing the integration over Ω_k and the sum over λ. If we now make the approximation $\omega = \omega_a - \omega_b$, we obtain the result

$$\Gamma^{SR}_{ab,\,ab} = \frac{4}{3\hbar c^3} \sum_{a'' \neq a} (\omega_a - \omega_{a''})^3 \left| \left\langle a \left| \vec{D} \right| a'' \right\rangle \right|^2 \theta(\omega_a - \omega_{a''})$$

$$+ \frac{4}{3\hbar c^3} \sum_{b'' \neq b} (\omega_b - \omega_{b''})^3 \left| \left\langle b \left| \vec{D} \right| b'' \right\rangle \right|^2 \theta(\omega_b - \omega_{b''}), \tag{63}$$

where

$$\theta(x) = \begin{cases} 1 & x > 1 \\ 0 & x < 1 \end{cases}, \tag{64}$$

which is the sum of all spontaneous emission rates out of the states a and b comprising the spectral line.

The contribution from all induced radiative transitions is conventionally expressed in terms of the specific intensity $I_\lambda(\omega, \ )$ which is related to the average number of photons by

$$\left\langle n_\lambda (\omega, \Omega) \right\rangle = \frac{8\pi^3 c^2}{\hbar \omega^3} \quad I_\lambda \ (\omega, \Omega). \tag{65}$$

If we again make the approximation $\omega = \omega_a - \omega_b$, we obtain the result

$$\Gamma^{IR}_{ab,\,ab} = \frac{4\pi^2}{\hbar^2 c} \sum_\lambda \int d\Omega_k \Bigg\{ \tag{66}$$

$$\sum_{a'' \neq a} \left| \left\langle a \left| D \right| a'' \right\rangle \right|^2 \left[I_\lambda(\omega_a - \omega_{a''}, \Omega_k)\theta(\omega_a - \omega_{a''}) + I_\lambda(\omega_{a''} - \omega_a, \Omega_k)\, \theta\, (\omega_{a''} - \omega_a) \right]$$

$$+ \sum_{b'' \neq b} \left| \left\langle b \left| D \right| b'' \right\rangle \right|^2 \left[I_\lambda(\omega_b - \omega_{b''}, \Omega_k)\theta(\omega_b - \omega_{b''}) + I_\lambda(\omega_{b''} - \omega_b, \Omega_k)\theta\ (\omega_{b''} - \omega_b) \right] \Bigg\},$$

which gives the contribution to the width from all stimulated radiative emission and absorption processes out of the states a and b. Results similar to those

given by equations (63) and (66) have also been obtained by Lambropoulos[11]. The starting point in his work is the autocorrelation function.

C. Collisions

The contribution to equation (58) from collisions between the perturbers and the radiating atomic system is given by

$$\Gamma^{c}_{a\,b\,,\,a\,b}(\omega) = \frac{2\pi}{\hbar^2} \sum_{a'' \neq a} \sum_{p''} \sum_{p} \left| \left\langle a\ p \left| V^{S\,P} \right| a''\ p'' \right\rangle \right|^2$$

$$\times\ \delta\ (\omega - \omega_{a''} + \omega_b - \omega_{p''} + \omega_p)\ \rho_p$$

$$+ \frac{2\pi}{\hbar^2} \sum_{b'' \neq b} \sum_{p''} \sum_{p} \left| \left\langle b\ p \left| V^{S\,P} \right| b''\ p'' \right\rangle \right|^2$$

$$\times\ \delta\ (\omega - \omega_a + \omega_{b''} - \omega_p + \omega_{p''})\ \rho_p \qquad (67)$$

$$+ \frac{2\pi}{\hbar^2} \sum_{p} \sum_{p'} \left| \left\langle a\,p \left| V^{S\,P} \right| a\,p' \right\rangle - \left\langle b\ p \left| V^{S\ P} \right| b\ p' \right\rangle \right|^2$$

$$\times\ \delta\ (\omega - \omega_a + \omega_b - \omega_{p'} + \omega_p)\ \rho_{p'}\ .$$

We now treat electron collisions in the binary-collision approximation, and set $\omega = \omega_a - \omega_b$, which corresponds to the impact approximation in the theory of spectral line broadening[13].

It is conventional in electron-atom collision theory to introduce the inelastic scattering cross section

$$\sigma\ (a \rightarrow a'',\ \vec{p}) = \frac{2\pi}{\hbar^2 V_e} \sum_{p''} \left| \left\langle a\,\vec{p} \right| V^c \left| a''\,\vec{p}'' \right\rangle \right|^2 \delta\ (\omega_a - \omega_{a''} - \omega_{p''} + \omega_p) \quad (68)$$

and the elastic scattering amplitude

$$f_a(\vec{p},\ \vec{p}'') = -\frac{m_e}{2\pi\hbar^2} \left\langle a\,\vec{p} \right| V^c \left| a\,\vec{p}'' \right\rangle \quad , \quad (69)$$

where $\vec{p}$ denotes the wave vector describing the electron scattering by the atomic system, and V^c is the appropriate collisional interaction. These quantities can be defined without the use of lowest-order perturbation theory by replacing V^c by the scattering matrix T.

The isolated-line width produced by electron collisions is then obtained in the form

$$\Gamma^c_{a\,b,\,a\,b} = N_e \sum_{\vec{p}} \rho\ (\vec{p}) \left\{ \sum_{a'' \neq a} V_e\ \sigma\ (a \rightarrow a'',\ \vec{p}) + \sum_{a'' \neq b} V_e\ \sigma\ (b \rightarrow b'',\ \vec{p}) \right.$$

$$\left. + V_e \int d\Omega_{p''} \left| f_a\ (\vec{p},\ \vec{p}'') - f_b\ (\vec{p},\ \vec{p}'') \right|^2 \right\} \quad , \quad (70)$$

where N_e is the electron density and V_e is the electron velocity. The density matrix $\rho\ (p)$ corresponds to the electron velocity distribution. This result is in agreement with the work of Baranger[1-3]. Note that the total width due to collisions is the sum of the rates for all inelastic transitions and a term involving the square of the difference between the elastic scattering amplitudes.

We have shown that the approximation of R(z) by $\mathcal{V}$ implies that the isolated line width can be obtained by adding up the partial widths arising from auto-ionization, spontaneous and induced radiative transitions, and collisions, as expressed by equations (60), (64), (66), and (70).

$$\Gamma_{a\,b,\,a\,b} = \Gamma^{A}_{ab,\,ab} + \Gamma^{SR}_{ab,\,ab} + \Gamma^{IR}_{ab,\,ab} + \Gamma^{C}_{a\,b,\,a\,b} \qquad (71)$$

Although the final results have been worked out explicitly in the approximation $\omega = \omega_a - \omega_b$, it should be emphasized that the general theory predicts that each partial width will have a frequency dependence.

5. RELATIVE IMPORTANCE OF VARIOUS BROADENING MECHANISMS

In order to determine the relative importance of various broadening mechanisms for a particular spectral line, the expressions obtained for the isolated line widths in section IV must be evaluated using realistic atomic wavefunctions. In this section, we discuss approximate evaluations of the widths which reveal their dependence on the states a and b comprising the line and on the physical properties of the surrounding particles and radiation field. The shifts, which are not considered in this investigation, may be important, particularly in the case of induced transitions.

Even when the atomic lines are assumed to be isolated, the upper and lower levels a and b usually consist of degenerate magnetic sublevels. The result of superimposing the contributions from each allowed magnetic component can be shown[13,17] to be the same as the expression obtained from equation (45) after both $|\vec{D}_{a\,b}|^2$ and $\mathcal{R}_{a\,b,\,a\,b}(\omega)$ are summed over the magnetic sublevels of b and averaged over the magnetic sublevels of a. The density matrix ρ_a must be replaced by the number density of atoms in the state a, regardless of the magnetic sublevel quantum numbers. In the remainder of this section, all atomic states will be specified by giving only the principal and angular momentum quantum numbers of the active electron.

A. Autoionization

Consider the autoionizaton process corresponding to the ejection of an $n\ell$-electron accompanied by the deexcitation $n_a\ell_a \rightarrow n_c\ell_c$ of one of the remaining bound electrons. Using quantum-defect theory[21], the autoionization rate for large n can be related to the cross section for the excitation $n_c\ell_c \rightarrow n_a\ell_a$ induced by electron impact. In a previous paper[22], we showed that the autoionization rate due to the dipole part of the electrostatic interaction can be approximated by

$$A_a(n_a\ell_a, n\ell \rightarrow n_c\ell_c) = \frac{E_H}{\hbar}\left(\frac{8\pi}{\sqrt{3}}\right)\left(\frac{2Z^2}{\pi n^3}\right)\frac{2(2\ell_c+1)}{2(2\ell_a+1)\ 2\ (2\ell+1)}$$
$$\left(\frac{E_H}{E_a-E_c}\right) f(n_c\ell_c \rightarrow n_a\ell_a) \sum_{\ell'} g(\epsilon_c\ell' \rightarrow \epsilon_a\ell)\Big|_{\epsilon_a = 0}, \qquad (72)$$

where $f(n_c\ell_c \rightarrow n_a\ell_a)$ is the oscillator strength and $g(\epsilon_c\ell' \rightarrow \epsilon_a\ell)\big|_{\epsilon_a = 0}$ is the threshold value of the partial-wave Gaunt factor for the free-free transition of an electron in the field of the ion with residual charge Z. In the non-relativistic approximation employed here, equation (70) is practically independent of Z. The n^{-3} dependence which is predicted is a well-known property. The ℓ-dependence is difficult to derive, but experience in evaluating the free-free Gaunt factor indicates that the autoionization rates decrease rapidly with increasing ℓ, typically like ℓ^{-5}.

B. Spontaneous Radiative Transitions

The properties of radiative transition rates are so well-known that only a brief discussion will be necessary. Using the asymptotic behavior of the hydrogenic oscillator strengths for large n, the spontaneous radiative decay rate due to all downward transitions can be estimated by[23]

$$A_r(n) = 1.6 \times 10^{10} \frac{Z^4}{n^{9/2}} \quad \text{sec}^{-1} \quad . \tag{73}$$

It should be kept in mind that equation (73) describes only $\Delta n \neq 0$ transitions, for which the radiative decay rates increase like Z^4 with increasing Z. The $n^{-9/5}$ dependence indicates that the dominant radiative decay mode for a doubly-excited state with the outer-electron in a high-n level will be the radiative deexcitation of the inner-electron.

The total spontaneous radiative width is estimated by

$$\Gamma^{SR}_{ab,\,ab} = 1.6 \times 10^{10}\, Z^4\, (n_a^{-9/2} + n_b^{-9/2}) \ , \tag{74}$$

with the understanding that n_a and n_b refer to the lowest values for which a dipole transition can occur.

In medium- and high-Z ions, the most prominent emission lines have radiative decay rates which are at least comparable to any autoionization rates. Consequently, equation (74) can be used as an estimate for the total natural width. It should be emphasized that prominent absorption lines can arise from transitions to autoionizing levels whose spontaneous radiative decay rates are relatively small.

C. Induced Radiative Transitions

The result obtained after averaging equation (66) over the magnetic quantum numbers can be written in the single-particle approximation as

$$\Gamma^{IR}_{ab\,,\,ab} = \frac{4\pi^2 e^2}{3\hbar^2 c} \left\{ \sum_{\lambda} \int d\Omega_k \right.$$

$$\sum_{n_{a''}\ell_{a''} \neq n_a \ell_a} \frac{\max(\ell_a, \ell_{a''})}{(2\ell_a + 1)} \left| \left\langle n''_a \ell''_a \left| r^2 \right| n_a \ell_a \right\rangle \right|^2$$

$$\times \left[I_\lambda(\omega_a - \omega_{a''}, \Omega_k)\, \Theta(\omega_a - \omega_{a''}) + I_\lambda(\omega_{a''} - \omega_a, \Omega_k)\, \Theta(\omega_{a''} - \omega_a) \right] \tag{75}$$

$$+ \sum_{n_{b''}\ell_{b''} \neq n_b \ell_b} \frac{\max(\ell_b, \ell_{b''})}{(2\ell_b + 1)} \left| \left\langle n_{b''}\ell_{b''} \left| r^2 \right| n_b \ell_b \right\rangle \right|^2$$

$$\left. \times \left[I_\lambda(\omega_b - \omega_{b''}, \Omega_k)\, \Theta(\omega_b - \omega_{b''}) + I_\lambda(\omega_{b''} - \omega_b, \Omega_k)\, \Theta(\omega_{b''} - \omega_b) \right] \right\}$$

We note that the electron impact width associated with inelastic transitions can be obtained in the Bethe approximation from equation (75) simply by replacing $\frac{1}{c} \sum_{\lambda} \int I_\lambda(\omega, \Omega)\, d\Omega$ by $e^2 N_e \int \frac{f(V_e)}{V_e} \frac{2g}{\sqrt{3}}$.

The application of the r^2 sum rules given by Bethe and Salpeter[24] is prevented by the photon-frequency dependence of the radiation field intensity $I_\lambda(\omega, \Omega)$. If we define a total intensity by

$$I(\omega) = \sum_{\lambda} \int d\Omega_k\, I_\lambda(\omega, \Omega_k) \tag{76}$$

and replace $I(\omega)$ by a suitable frequency-independent average intensity I, the summations over the complete sets of states $n_{a''}\ell_{a''}$ and $n_{b''}\ell_{b''}$ can be carried out, and the absorption and stimulated emission contributions can be combined to give the result

$$\Gamma^{IR}_{a\,b\,,a\,b} = \frac{4\pi^2 e^2}{3\hbar^2 c}\,\bar{I}\left[\left\langle n_a \ell_a \left| r^2 \right| n_a \ell_a \right\rangle + \left\langle n_b \ell_b \left| r^2 \right| n_b \ell_b \right\rangle\right]. \qquad (77)$$

The expectation values of r^2 will now be approximated by using the hydrogenic formula

$$\left\langle n\ell \left| r^2 \right| n\ell \right\rangle = \frac{n^2}{2Z^2}\left(5n^2 + 1 - 3\ell\,(\ell+1)\right) a_o^2 \qquad (78)$$

$$\simeq \frac{2n^4}{Z^2}\, a_o^2 \quad ,$$

where the last version corresponds to an ℓ-independent approximation.

Let us consider a thermal equilibrium distribution of radiation characterized by a radiation temperature T_R. We assume that this radiation is incident from one side only, so that the integration over Ω_k reduces to multiplication by 2π. We choose the frequency-independent intensity

$$\bar{I} = \frac{(k T_R)^3}{2\pi^2 c^2 \hbar^2} \quad , \qquad (79)$$

which is about 2/3 the maximum value of the Planck distribution function corresponding to T_R. The estimated width due to induced radiative transitions is then given by

$$\Gamma^{IR}_{ab,\,a\,b} = \frac{\alpha^3}{3}\left(\frac{E_H}{\hbar}\right)\left(\frac{kT_R}{E_H}\right)^3\left(\frac{n_a^4 + n_b^4}{Z^2}\right) \qquad (80)$$

$$= 2.67 \times 10^9 \left(\frac{kT_R}{E_H}\right)^3\left(\frac{n_a^4 + n_b^4}{Z^2}\right) \quad \text{sec}^{-1}.$$

In contrast to equation (74) for $\Gamma^{SR}_{ab,\,ab}$, $\Gamma^{IR}_{ab,\,ab}$ increases with increasing principal quantum number and decreases with increasing residual charge. The $(k\,T_R)^3$ dependence on the radiation temperature is also an important property.

Unless the induced radiative transitions have frequencies within the region of the maximum in $I(\omega)$, equation (80) is probably an overestimate of the actual width.

D. Electron Collisions

It has been pointed out by Griem[25] that the Bethe approximation for the electron-impact width due to inelastic transitions can be modified to take into account some of the effects of elastic scattering. This is done by beginning the integral over the Maxwellian distribution at zero velocity rather than starting it at the excitation threshold. The result can be written as

$$\Gamma^{C}_{a\,b,\,a\,b} = \frac{32}{3\sqrt{3}}\,\pi^{3/2}\,a_o\,N_e\left(\frac{E_H}{\hbar}\right)\sqrt{\frac{E_H}{kT_e}}\Bigg\{ \tag{81}$$

$$\sum_{n_a''\,\ell_a'' \neq n_a\ell_a} \frac{\max(\ell_a'',\ell_a)}{(2\ell_a+1)}\left|\left\langle n_a''\ell_a''\left|r^2\right|n_a\ell_a\right\rangle\right|^2 g\left(\frac{3kT_e}{2|E_a''-E_a|}\right)$$

$$\sum_{n_b''\,\ell_b'' \neq n_b\ell_b} \frac{\max(\ell_b'',\ell_b)}{(2\ell_b+1)}\left|\left\langle n_b''\ell_b''\left|r^2\right|n_b\ell_b\right\rangle\right|^2 g\left(\frac{3kT_e}{2|E_b''-E_b|}\right)\Bigg\},$$

where g now denotes the thermal average of the free-free Gaunt factor.

If the Gaunt factors in equation (81) are now replaced by suitable average values, the r^2 sum rules can be employed to obtain the result[25]

$$\Gamma^{C}_{ab,\,ab} = \frac{3\,2}{3\sqrt{3}}\,\pi^{3/2}\,a_o\,N_e\left(\frac{E_H}{\hbar}\right)\sqrt{\frac{E_H}{kT}}$$

$$X\left\{\left|\left\langle n_a\,\ell_a\,\middle|\,r^2\,\middle|\,n_a\,\ell_a\right\rangle\right|\,g\left(\frac{3kT_e}{2\Delta E_a}\right)\right. \tag{82}$$

$$\left.\left|\left\langle n_b\,\ell_b\,\middle|\,r^2\,\middle|\,n_b\,\ell_b\right\rangle\right|\,g\left(\frac{3kT_e}{2\Delta E_b}\right)\right\}$$

where ΔE_a and ΔE_b should be chosen to be the smallest threshold energies. We now use equation (78) and set the average Gaunt factors equal to unity, which is a good approximation for $\Delta n=0$ transitions in multiply-charged ions. The electron impact width is then estimated by

$$\Gamma^{C}_{ab,\,ab} = \frac{6\,4}{3\sqrt{3}}\,\pi^{3/2}\,a_o^{\,3}\,N_e\left(\frac{E_H}{\hbar}\right)\sqrt{\frac{E_H}{kT_e}}\,\left(\frac{n_a^{\,4}+n_b^{\,4}}{Z^2}\right)$$

$$= 2.1\times 10^{-7}\,N_e\sqrt{\frac{E_H}{kT_e}}\,\left(\frac{n_a^{\,4}+n_b^{\,4}}{Z^2}\right)\,. \tag{83}$$

As expected, the electron impact width has the same n- and Z- dependences as the width due to induced radiative transitions. The ℓ-dependences would also be the same if they had been retained in the approximation for the expectation values of r^2. The condition for thermal radiation broadening to be dominant over electron impact broadening is found from equations (80) and (83) to be

$$\left(\frac{kT_R}{E_H}\right)^3 > 7.9\times 10^{-17}\,N_e\sqrt{\frac{E_H}{kT_e}}\,. \tag{84}$$

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